Extended Abstract

Nominations 2023 – EFCE Young Researcher Award in Mixing

PhD Thesis: "Mixing Mechanisms in 2D Reactors"

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Summary

The thesis entitled "Mixing Mechanisms in 2D reactors" aims at the identification and the characterisation of the mixing mechanisms in 2D reactors. The 2D nature of flow and mixing in these reactors stems from the fact that the mixing dynamics are well-represented by 2D time-dependent maps, and the energy transfer mechanisms between flow scales are described from bidimensional turbulence. The 2D mixers/reactors in this thesis are rotational devices, Split-and-Recombine (SR) mixers, Confined Impinging Jets (CIJ) and T-Jets mixers.

Rotational devices are suggested as small-scale batch laboratory mixers. These devices can replicate industrial mixing conditions in 2D reactors, which have a great application in rapid formulation processes.

Mixing evolution of dissimilar fluids was assessed in CIJ and T-Jets mixers from experimental data for a viscosity ratio range from 2 to 10 and different densities. Results show that CIJ and T-Jets mixers can promote the efficient mixing of dissimilar fluids under a chaotic flow regime. A Kinetic Energy Model (KEM) is proposed as a universal design equation to predict the impingement point position of the opposed jets in CIJ mixers. For T-Jets mixers, an elastic analogue of the two inlet jets is proposed to describe this position. The validation of these models from experimental and numerical results indicates that these analytical expressions can be used as design tools for industrial opposed jets mixers, both CIJ and T-jets. An industrial case-study was considered for the validation of the analytical model in CIJ mixers: the continuous emulsification process (e.g. the production of mayonnaise).

This thesis also proposes an explicit and straightforward design expression to calculate the striation thickness decay, which is the limiting step in mixing operation in SR mixers. This design methodology has never been demonstrated and explains the results in the literature. Its validation from Computational Fluid Dynamics (CFD) simulations showed that this model could be implemented as a design tool for industrial SR mixers.

This thesis brings more advances in the know-how on 2D reactors, contributing to the generation of useful data and solutions for robust experimental designs based on the fundamental understanding of mixing mechanisms. The long-term objective of this work is the collection of design tools to implement 2D reactors in plants and on product development methodologies targeted at these mixers.

Problem Addressed

Two problems were addressed in this thesis. The first one regards mixing dissimilar fluids in opposed jets mixers, which is an important aspect that has not been approached systematically. In fact, the German company KraussMaffei has already engaged in a successful industrial demonstration with LSRE-LCM research team regarding a mixing process in a CIJ mixing chamber for two fluids with a viscosity ratio of 10. However, mixing science that enabled the efficient and fast mixing of dissimilar fluids was based on works with similar fluids at different flow rate ratios (Fonte et al., 2016).

Another industrial challenge is the scaled-up from the product development stage to the industrial process. Mixing conditions at industrial units are not easily mimicked at lab scale because the lab devices promote intensive mixing conditions that do not occur at the industrial scale. The inefficient mimicking of mixing conditions at the lab scale usually leads to the failure of the formulation recipe in the production stage of complex chemical products.

State of the Art

Experimental and numerical studies on the fundamentals of mixing provided evidence of an interesting particularity of CIJ and T-Jets mixers: the 2D nature of the flow dynamics and mixing. The small and micro-sized dimensions of these reactors (meso and microreactors) ensure that mixing occurs at laminar flow regimes, and it is mainly enhanced by chaotic fluid motion. The flow dynamics at chaotic flow regimes causes the fast elongation of fluid elements and reduces the length scales, which occurs at the same rate as the stretching. Thus, the flow dynamics is defined by a 2D time-dependent map (Mohr et al., 1957; Chien et al., 2006). In 2D flows where the main mixing mechanism is the generation of the interfacial area between the flow streams, the energy injection from flow into mixing is efficient, and the mixing mechanisms are better controlled. This opens an exciting prospect in terms of energy efficiency and product quality in industrial processes.

Furthermore, the energy transfer between flow scales in 2D reactors is well-described within the framework of the 2D turbulence theory. In this theory, the energy is injected from smaller scales, approximately with the dimensions of feed flow streams, and then it is fed to larger eddies, with roughly the dimension of the reactor diameter or width (Gonçalves et al., 2017). Based on 2D time-dependent maps and 2D turbulence theory arguments, mixers in this thesis are considered 2D.

The first descriptions of mixing were analysed under shear flows, which occur in purely laminar systems. Two parameters can be used as metrics for the mixing degree: the generation of interfacial area (Spencer and Wiley, 1951) and the striation thickness (Mohr et al., 1957). Mohr et al. (1957) introduced the concept of striation thickness from the visualisation of a dye dispersed into a fluid and enclosed between two parallel plates. The top plate is moving, and both fluids have the same viscosity and density, and the diffusion between them was neglected.

The result is the stretching of dye and the increase of the interfacial area between the representative fluids. The visualisation of motion shows the creation of thin lamellae of dye, whose width is the striation thickness. This experiment showed that the deformation field and the orientation of fluid elements significantly impact laminar mixing. This promotes the increase of the interfacial area and enhances the concentration gradients by reducing the striation thickness.

In shear flows, stretching creates a linear growth of the interfacial area for a long time (Ottino and Wiggins, 2004). However, the interface growth can be empowered in a chaotic flow regime. Ottino (1989) describes the mechanical mixing in chaotic flows as the stretching and folding, in space and time, of an element of fluid tracked in the system.

Key innovations

Five key innovations can be highlighted:

i. Rotation devices are proposed as a methodology for screening the 2D mixing information generated in mesoreactors. The mixing scales are fully controlled by the velocity of the top plate and the number of turns;
ii. An analytical equation is proposed to describe the impingement point position (IP) in a CIJ mixing chamber. This equation takes into account the geometrical parameters, the velocity of jets and the physical properties of fluids. Therefore, the validation addressed in this thesis has a huge contribution to the design of industrial processes in CIJ mixers;
iii. The applications of CIJ mixers were also extended to a continuous emulsification process. The efficient mixing is promoted by injecting the dispersed and the continuous phases as two opposed jets. In this process, the energy dissipation at IP promotes the effective mixing between phases;
iv. A design equation and the respective validity range were also proposed to describe the IP position in the T-Jets mixing chamber;
v. An analytical equation that describes the striation thickness decay is proposed as a design tool for SR mixers. The full description of the mixing mechanisms involved in this method expands the opportunity to apply SR mixers for process intensification.

Applications

The results of this work have a wide range of industrial applications. Static mixers are especially suited for applications where flow rates are too low (e.g. microfluidic applications) or viscosity is too large (e.g., food, coatings, cosmetic, polymer adhesive and detergent industries). In the particular case of CIJ and T-Jets mixers, fundamental studies on mixing enable the generation of useful data to design experiments/processes in these devices (e.g. the production of polyurethanes in CIJ mixers; the production of nanoparticles in T-Jets mixers). This work also shows that CIJ mixers can be used for other intensive mixing applications, such as continuous emulsification processes, by injecting the dispersed and continuous phases as two opposed jets. Finally, rotational devices proposed in this thesis can be applied in a wide range of formulation processes, particularly in industrial processes that involve fast polymerisation reactions (e.g. the production of polyurethanes in RIM machines).

Implementations and Results

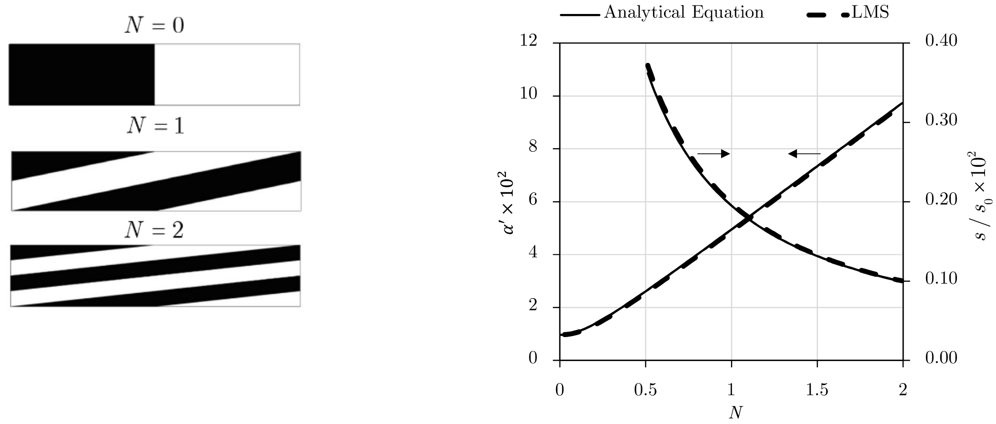
The results of this thesis were divided into four parts.

High Throughput Material Development in Rotational Devices

Mixing in rotational devices was studied from 3D CFD simulations using ANSYS Fluent. The rotational device consists of two parallel plates, a rotating top plate and a stationary bottom plate. The sidewalls have zero shear stress conditions. The working fluids were two similar fluids, and mixing was simulated setting the Volume-Of-Fluid model. The two fluids are initially side by side. CFD results show that the rotation of the top plate promotes the stretching of the interface between phases, and the formation of a lamellar structure by the overlapping of phases. These results agree with the stretching of a dye in a laminar flow reported by Mohr et al. (1957). Mixing scales were quantified from 2D Lagrangian Mixing Simulations (LMS), a methodology proposed by Matos et al. (2018). The 2D geometry addressed consists of the outer circle of the plate-plate rotational device, i.e., two parallel walls. Periodic flow conditions were set at the sidewalls to simulate a continuous flow in the entire domain. Figure 1a shows the 2D contour maps at the initial time ($N = 0$), after one ($N = 1$) and two turns ($N = 2$). A similar lamellar structure is formed in 2D and 3D CFD models, validating the 2D simulations.

A method that tracks an infinitesimal element stretched in a shear flow was implemented to calculate the striation thickness decay. For that, an incompressible fluid was considered, and the striation thickness is given by $s(t)/s_0 = 1/\sqrt{1+\left(\frac{\omega R_P t}{h_P}\right)^2}$, where s_0 is the initial striation thickness at $t = 0$, h_P is the gap between the two parallel plates, ω is the angular velocity of the top plate in rad s^{-1} and R_P is the radius of the top plate. Figure 1b shows that the analytical expression fits well with the 2D CFD results. The validation of this expression enables to design operation conditions, such as the velocity of the top plate and the number of rotations, to achieve the desired striation thickness in the formulation process. The expression that describes the generation of the interfacial area was also demonstrated using the same methodology, and it is given by $\alpha'(t) = \sqrt{1+\left(\frac{\omega R_P t}{h_P}\right)^2}$.

CFD results show that rotational devices promote the laminar mixing between phases by stretching their interface. These rotational devices are easily adapted for different working conditions in the development of new materials, such as in polyurethane production sites, to make kinetic studies for the setup of RIM machines. RIM processes are usually designed in pilot machines, becoming a quite-consuming time process. The screening of 2D mixing information generated in the RIM machines mixing chamber (CIJ mixer) is successfully made from the identification of striation thickness decay in each deformation region. Figure 2 shows the analytical expressions of the angular speed at the top plate that promotes the mimicking of the same mixing conditions generated in each region of a CIJ mixing chamber (pancake shearing, engulfing vortices and CIJs runner).



(a) (b)

Figure 1. (a) Contour maps of 2D CFD results at the initial time ($N = 0$), after one ($N = 1$) and two turns ($N = 1$); (b) striation thickness evolution and interfacial area growth calculated from LMS and analytical equations.

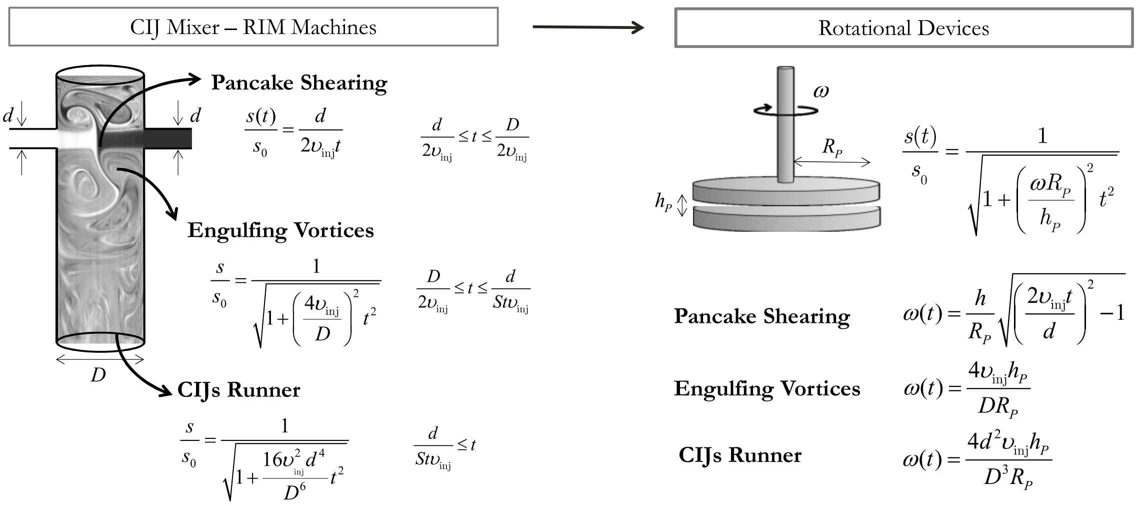
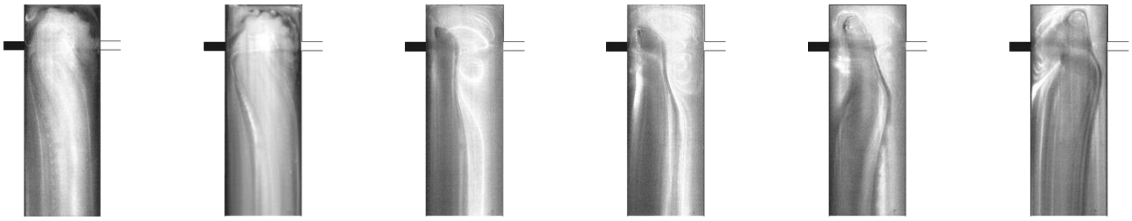


Figure 2. Mixing scales length evolution in CIJ mixers and related evolution in a plate-plate rheometer.

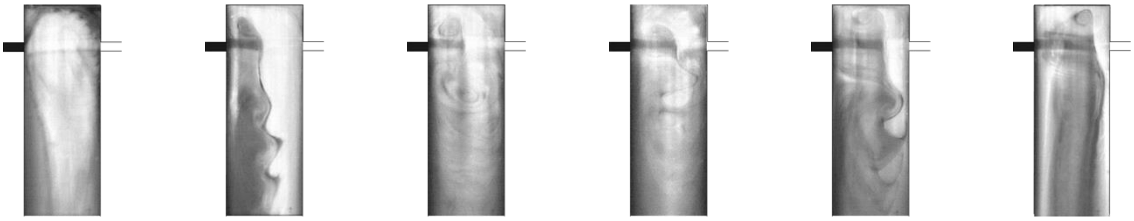
Mixing Mechanisms in Confined Impinging Jets Mixers

CIJ mixers are commonly applied in industrial processes to mix two dissimilar fluids, i.e. fluids with different densities and viscosities. Experimental and numerical studies show that CIJ mixers are able to mix efficiently dissimilar fluids under a self-sustainable chaotic flow regime. Figures 3 and 4 show Planar Induced Laser Fluorescence (PLIF) images obtained at the plane defined by the mixing chamber and injectors axes, for a viscosity ratio 5 at two Reynolds numbers, $\mathrm{Re}_2 = 50$ and $\mathrm{Re}_2 = 70$. The two liquid streams are aqueous solutions of glycerol, and the refraction indices were matched using calcium chloride. Rhodamine 6G was used as marker in PLIF experiments. Indices 1 and 2 in Re_1 and Re_2 correspond respectively to the left-hand-side and right-hand side injectors. The less viscous (LV) fluid was injected through injector 1, and the more viscous (MV) fluid through the opposed injector.



(a) (b) (c) (d) (e) (f)

Figure 3. PLIF images for a viscosity ratio 5 $\mathrm{Re}_2 = 50$ using Chamber 1 and at (a) $\mathrm{Re}_1 = 114$; (b) $\mathrm{Re}_1 = 125$; (c) $\mathrm{Re}_1 = 154$; (d) $\mathrm{Re}_1 = 154$; (e) $\mathrm{Re}_1 = 211$; (f) $\mathrm{Re}_1 = 248$.

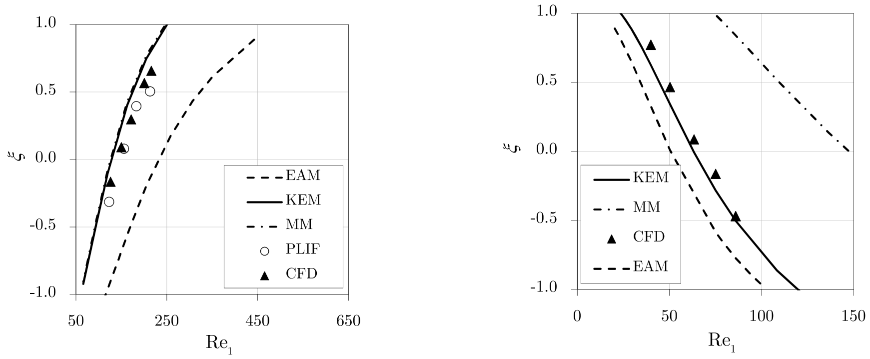


(a) (b) (c) (d) (e) (f)

Figure 4. PLIF images for a viscosity ratio 5 at $\mathrm{Re}_2 = 70$ using Chamber 1 and at (a) $\mathrm{Re}_1 = 168$; (b) $\mathrm{Re}_1 = 243$; (c) $\mathrm{Re}_1 = 250$; (d) $\mathrm{Re}_1 = 289$; (e) $\mathrm{Re}_1 = 303$; (f) $\mathrm{Re}_1 = 350$.

Figures 3 and 4 show that the necessary conditions for effective mixing are the balance of jets, and the critical Reynolds number ($\mathrm{Re}_c > 150$), which is defined by the MV stream conditions. These results also show that the viscosity ratio plays a critical role in the onset of chaotic flow regimes for mixing dissimilar fluids in CIJ mixers.

The accurate description of IP position in the CIJ mixing chamber enables the design of experiments/processes in these devices. Three models were considered for the description of the IP position in the mixing chamber: elastic analogue model (EAM), kinetic energy model (KEM) and momentum model (MM). These models take into account the physical properties of fluids, the conditions at the inlets and geometrical parameters. EAM, which is based on the analogy of two jets and two springs, was proposed by Fonte et al. (2016), and it gives a good prediction of the IP position for mixing similar fluids. KEM and MM are proposed for the first time in this thesis and are based on the balance of kinetic energy and momentum of jets at IP position, respectively. Experimental and numerical results were used to validate EAM, KEM and MM. Figure 5 shows the dimensionless IP position, ξ, determined from experimental and numerical results for two different conditions: a viscosity ratio of 5 and density ratio 1; and a viscosity ratio of 5 and a density ratio of 10. Figure 5 shows that KEM is the General Design Equation (GDE) equation because it has a broader validity range.



(a) (b)

Figure 5. Dimensionless IP point determined from EAM, KEM, MM. CFD results and PLIF data for the mixing of dissimilar fluids with viscosity ratio 5 and (a) density ratio of 1 and $\mathrm{Re}_2 = 45$ and (b) density ratio of 10 and $\mathrm{Re}_2 = 45$.

The validation of KEM as a GDE enables a more efficient design of experiments in CIJ mixers. This model was used to design a continuous emulsification process in CIJ mixers. Sunflower oil and an aqueous solution of 1.3% wt/wt of lecithin, the emulsifier, were injected as two opposed jets in the mixing chamber. The design of experiments was based on the previous results: the Reynolds number of the MV fluid (sunflower oil) was defined above the critical Reynolds number, and the opposed injector conditions were determined from KEM for $\xi = 0$, which corresponds to the balanced flow conditions. Droplet size distribution was obtained from microscope images of an emulsion sample collected at the outlet of the mixing chamber. The droplet size distribution was then compared with the emulsions produced in a batch process operating at the same shear rate conditions. Figure 6 shows that an oil-in-water emulsion (o/w emulsion) is produced by blending oil and an aqueous solution of lecithin. Emulsions in CIJ mixers operating at $\mathrm{Re}_{\mathrm{oil}} = 150$ and $\mathrm{Re}_{\mathrm{oil}} = 200$ present a homogeneous oil droplet size distribution when compared to the batch process emulsions (see Figure 6). These results are in agreement with the efficient energy injection in 2D flows since this injection is concentrated at the interface between phases, at the IP point.

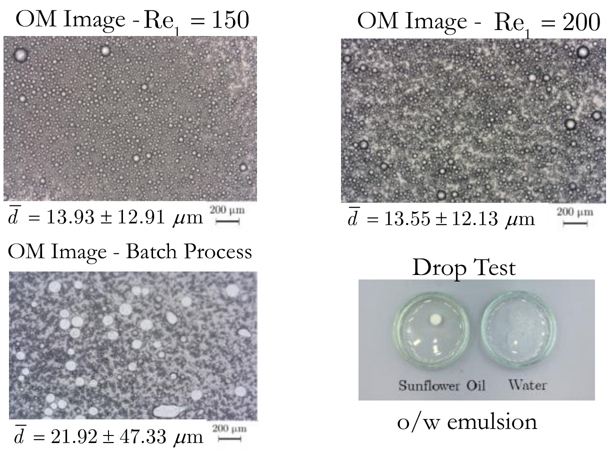


Figure 6. Optical Microscope images of emulsions produced in the continuous process for $\mathrm{Re}_{\mathrm{oil}} = 150$ and $\mathrm{Re}_{\mathrm{oil}} = 200$, in a batch process, the respective droplet diameter and photograph of the drop tests for o/w emulsions.

Mixing Mechanisms in T-Jets Mixers

Fundamental studies on mixing in T-Jets mixers only reported the critical conditions for the onset of a self-sustainable chaotic flow regime for similar fluids. The transition to the chaotic flow regime is strongly affected by Reynolds number and geometrical parameters. Previous works showed that the best geometrical configuration to the onset of the chaotic flow regime to mix two similar fluids is W6w1e4 (W=6mm, w=1mm and e=4mm). A sketch of this geometry is in Figure 7a.

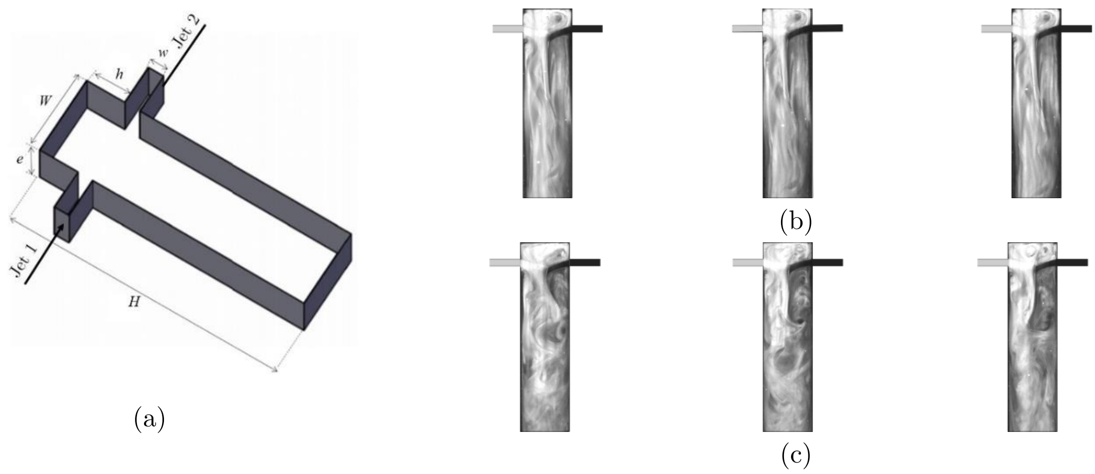


Figure 7. (a) Sketch of T-Jets mixers and respective dimensions; (b) PLIF images for mixing of two dissimilar with a viscosity ratio of 3 using geometry W6w1e4 at (b) $\mathrm{Re}_{\mathrm{Hjet1}} = 93$ and $\mathrm{Re}_{\mathrm{Hjet2}} = 560$; (c) $\mathrm{Re}_{\mathrm{Hjet1}} = 105$ and $\mathrm{Re}_{\mathrm{Hjet2}} = 640$.

This work extends the fundamental studies on mixing two dissimilar fluids in T-Jets mixers. The working fluids were aqueous solutions of glycerol, and rhodamine was used as marker. The MV fluid was injected through injector 1, and the LV fluid through injector 2 (see Figure 7a). The refraction indices of aqueous solutions of glycerol were matched using calcium chloride. Figures 7b and 7c show that the T-Jets mixers with a geometry W6w1e4 can mix two dissimilar fluids with a viscosity ratio of 3. The same conclusions were observed for a viscosity ratio of 1.2. PLIF images show that the transition to the self-sustainable chaotic flow regime is completely controlled by the jet with the lowest Reynolds number, the MV fluid, and jets' balanced conditions.

PLIF contour maps showed that shallower geometries do not promote the efficient mixing of phases due to the wall effects. Therefore, the geometrical parameters that enable the operation at chaotic flow regimes under symmetrical and unsymmetrical conditions at inlets are: $W / w = 6$ and $W / e \leq 2$.

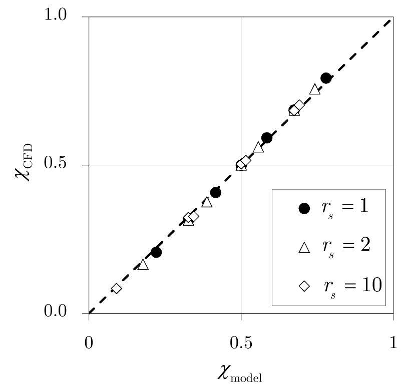
A model based on the analogy of two jets and two springs (elastic analogue model) was demonstrated to predict the offset of the IP position. This model takes into account the density of fluids and the velocity of jets. The validation of this model from CFD results showed that its validity range is: $-0.5 < \xi < 0.5$ and $\mathrm{Re} \geq 25$. The geometrical parameters considered in this validation were $W / w = 6$ and $W / e \leq 2$. This conclusion shows that the elastic analogue model can be used as a design tool for the balanced flow conditions, $\xi = 0$, which is the key condition for the transition to the self-sustainable chaotic flow regime.

Mixing Mechanisms in Split-and-Recombine Mixers

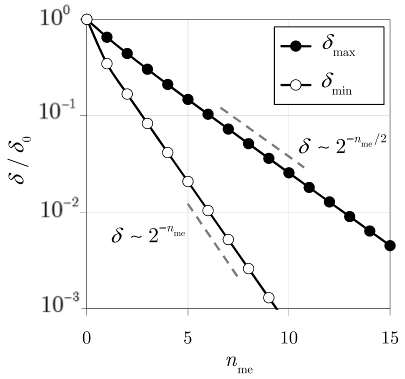
The flow in SR mixers was studied from a 3D CFD simulation using ANSYS Fluent. Mixing was simulated by setting the VOF model. The geometry addressed consists of a network of 4 converging "T"s. The two working fluids have the same physical properties and are injected at Stokes flow regimes. CFD results show that a non-homogeneous striation thickness distribution is formed at the outlet of each mixing element. The thinnest lamellae are stretched in the highest stretching region, i.e., in the centre of the channel, while the thickest lamellae are formed in the lowest stretching regions, i.e., close to the walls. The striation thickness distribution has the same shape as the velocity profile in a square section duct. The position of the interface between the two fluids was predicted from the mass balance in each mixing element, resulting in $\chi_i = \cos\left(\frac{1}{3}\cos^{-1}\left(1+4\chi_{i-1}^3-6\chi_{i-1}^2-\frac{2^{1-n_{me}} r_s^{a_0}}{r_s+1}\right)-\frac{2\pi}{3}\right)+\frac{1}{2}$, where r_s is the flow rate ratio, $i = 1$ to $2^{n_{me}+1}$, a_0 is 0 if i is even or 1 if i is odd and $\chi_0 = 0$. Figure 8a shows the validation of the analytical equation that describes χ_i and CFD results. This expression that describes the interface position enables the determination of the maximum and the minimum striation thickness: the maximum striation thickness decay is given by $\delta_{max}(n_{me}) = \cos\left(\frac{1}{3}\cos^{-1}\left(1-2^{-n_{me}}\right)-\frac{2\pi}{3}\right)+\frac{1}{2}$, and the minimum striation thickness is $\delta_{min}(n_{me}) = \cos\left(\frac{1}{3}\cos^{-1}\left(-2^{-n_{me}}\right)-\frac{2\pi}{3}\right)$.

The literature describes the mixing mechanisms in SR mixers from the repetition of the Baker's transformation, which consists of the cutting and re-stacking of the liquid streams. The creation of a multi-lamination structure in SR mixers promotes the reduction of the striation thickness, which is given by $\delta(n_{me}) = 2^{-(n_{me}+1)}$ in the light of the ideal transformation. Nevertheless, Figure 8b shows that the maximum and minimum striation thicknesses in SR mixers are given by $\delta_{max}(n_{me}) \sim 2^{-n_{me}/2}$ and $\delta_{min}(n_{me}) \sim 2^{-n_{me}}$. Therefore, the striation thickness of the largest scales in the flow decay half the rate of an idealised baker's transformation, showing that an SR mixer must be twice longer than an ideal mixer to achieve complete mixedness. The striation thickness decay has never been demonstrated in the literature, but it explains the experimental and numerical results in Neerincx et al. (2011) and Carrière (2007).

The main novelty of this work is the introduction of a new model to describe the non-homogeneous distribution of mixing scales in SR mixers. Results give an explicit and straightforward design expression to calculate the maximum striation thickness decay, which is the limiting step in mixing operation in this type of mixers.



(a)



(b)

Figure 8. (a) Parity plots comparing the interface positions obtained from the analytical model and the CFD simulations for different values of r_s after 2 mixing elements; (b) rate of mixing scales decay for $r_s = 1$ calculated for the thickness of the largest and smallest strips.

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